

A STUDY OF VIBRONIC COUPLING IN THE \bar{C} STATE OF CO_2^+

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RÉSUMÉ

Les effets du couplage vibronique dans l'état $\bar{C}(^2\Sigma_g^+)$ du CO_2^+ ont été étudiés pour des photons d'énergies comprises entre 20 et 28.5 eV. Deux analyseurs d'électrons hémisphériques suivis de détecteurs sensibles à la position combinés au rayonnement synchrotron de SURF-II ont permis une analyse vibrationnellement résolue de l'état $\bar{C}(^2\Sigma_g^+)$. La distribution angulaire caractérisée par le paramètre β de l'état vibrationnel interdit $\bar{C}(1,0,1)$ se révèle très différente de celle de l'état permis $\bar{C}(0,0,0)$. Les similarités entre la distribution angulaire (β vs. $h\nu$) de l'état interdit $\bar{C}(1,0,1)$ et celle de l'état $\bar{B}(^2\Sigma_u^+)$ supportent l'hypothèse de couplage vibronique entre ces deux états comme origine pour la bande interdite.

ABSTRACT

We have studied vibronic coupling in vibrationally resolved photoionization to the $\bar{C}(^2\Sigma_g^+)$ state of CO_2^+ in the photon-energy range $h\nu=20-28.5$ eV. The measurements utilize high-resolution hemispherical electron analyzers, equipped with area detectors, and the SURF-II synchrotron radiation source at the National Bureau of Standards. The angular distribution asymmetry-parameters (β) for the allowed $\bar{C}(0,0,0)$ and forbidden $\bar{C}(1,0,1)$ (19.747 eV binding energy) peaks are found to be quite different. However, similarities between the $\bar{C}(1,0,1)$ β curve and that for the \bar{B} state suggest that vibronic coupling to the $\bar{B}(^2\Sigma_u^+)$ state of CO_2^+ is the explanation for the intensity of the \bar{C} state forbidden band in the first 8 eV above threshold.

In the photoionization of small molecules, a symmetry-forbidden transition to the residual ion can sometimes occur. The intensity of such a transition can not be explained within the adiabatic and Franck-Condon approximations. One example of this effect is seen in the photoelectron spectrum of the fourth electronic state of CO_2^+ (\bar{C} , $^2\Sigma_g^+$, Fig. 1). The two vibrational peaks assigned as (0,1,0) and (1,0,1) are normally forbidden in photoionization from the fundamental neutral state. Their intensity has been explained by considering how the vibrational motion of the molecule couples together different electronic states in the final ion, an interaction termed vibronic coupling [1].

The aim of our work is to use branching ratios (B.R.) and angular distribution asymmetry parameters (β), measured as a function of the photoelectron's kinetic energy, to characterize the role of vibronic coupling in the \bar{C} state of CO_2^+ . Measurements were made with high-resolution photoelectron spectrometers (at $\theta=0^\circ$ and 90° with respect to the photon polarization direction) using synchrotron radiation from a 2 meter normal incidence monochromator at SURF-II (National Bureau of Standards) [2]. For this study, data were obtained with the electron spectrometers operating at two pass energies (2 and 5 V), with good agreement between data sets. The combined resolution of the light monochromator and the electron analyzer ranged from 36-60 meV and 53-75 meV for the 2 and 5 V pass spectra, respectively.

We emphasize here the β results for the $\bar{C}(0,0,0)$ and $\bar{C}(1,0,1)$ vibrational levels with binding energies of 19.387 and 19.747 eV,

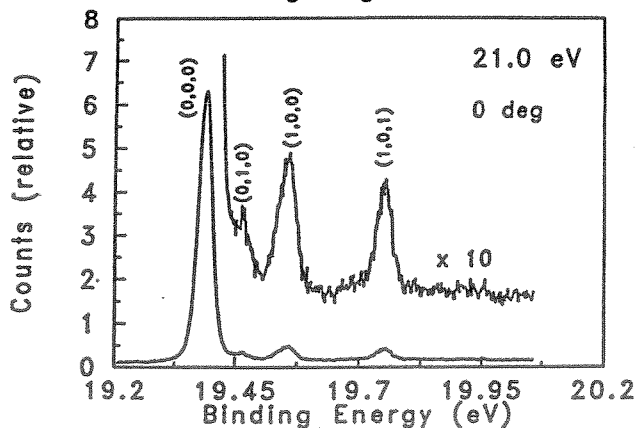


Figure 1: Photoelectron spectrum of the \bar{C} state of CO_2^+ taken at 21.0 eV photon energy, $\theta=0^\circ$, and 2 V pass energy.

respectively [3]. The assignment of the second peak as (1,0,1) is uncertain; (0,0,1) is also a possible assignment, as discussed by Baer et al. [3] and Veenhuizen et al. [4]. Previous work with He I resonance lamps indicates significant differences between $\beta(1,0,1)$ and $\beta(0,0,0)$ at $h\nu=21.2$ eV [4]. Our β results in Fig. 2 show that this difference persists in the first 8 eV above threshold. Although not shown here, the β results for the allowed (1,0,0) transition are, in contrast, generally quite similar to $\beta(0,0,0)$.

These trends emphasize the sensitivity of β to the subtle effects of vibronic coupling. Specifically, it has been proposed that in the vibronic coupling model of Domcke [1], the kinetic-energy dependence for the β curve of a symmetry-forbidden transition may mimic the β curve of the electronic state to which it couples. For either assignment of the 19.747 eV peak, when the electronic $\tilde{C}(^2\Sigma_g^+)$ and vibrational motions ($\nu_1=\Sigma_g$, $\nu_3=\Sigma_u$) are coupled, a combined total symmetry of Σ_u results. Assuming that the forbidden state derives intensity from the intense ν_1 levels of the available electronic states, we find that only the $\nu_1(\Sigma_g)$ modes of the $\tilde{B}(^2\Sigma_u^+)$ state combine to yield a total symmetry of Σ_u .

Thus, we show in Fig. 2 the experimental β results of Grimm et al. [5] for the (0,0,0) level of the \tilde{B} state of CO_2^+ plotted as a function of kinetic energy. The similarity to β for the $\tilde{C}(1,0,1)$

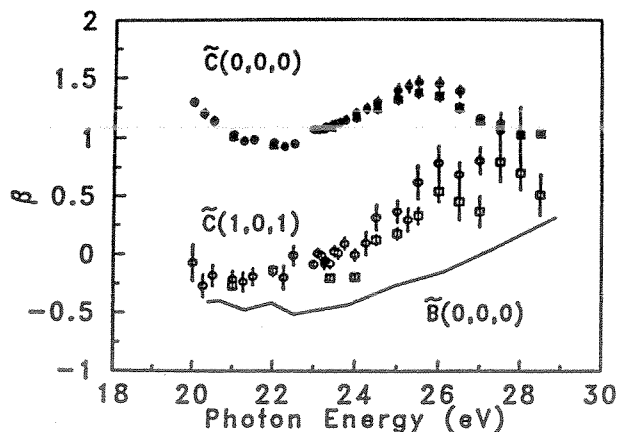


Figure 2: β results for the $\tilde{C}(0,0,0)$ and $\tilde{C}(1,0,1)$ vibrational levels of CO_2^+ . Results for 2 V (squares) and 5 V (circles) pass energy are shown. Experimental results of Grimm et al. [5] for the $\tilde{B}(0,0,0)$ state as a function of kinetic energy are connected by the solid curve.

level supports the role of vibronic coupling with the $\bar{B}(^2\Sigma_u^+)$ state. Additional effects such as variations in molecular geometry, shape resonances, and interchannel coupling will also contribute, in general, to the shape of the β curve for a forbidden band. These factors may explain the shift in absolute magnitude between the β curves for the forbidden band and the $\bar{B}(0,0,0)$ transition.

In summary, the similarity between the β curves for the \bar{C} state forbidden peak at 19.747 eV binding energy and the $\bar{B}(0,0,0)$ state of CO_2^+ suggests that vibronic coupling with the $\bar{B}(^2\Sigma_u^+)$ state is responsible for the intensity in the forbidden band. We have shown that in this case it is possible to identify the origin of the vibronic coupling from the β dependence of the forbidden peak. Theoretical work is needed to confirm this interpretation and the peak assignment, and experimental work in progress on all the vibrational levels of the \bar{C} state of CO_2^+ should help to elucidate general trends in the vibrationally-resolved ionization of this triatomic molecule.

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